SOME PHOTOELECTRIC AND THERMIONIC PROPERTIES OF RHODIUM

By E. H. Dixon
Department of Physics, University of Georgia

(Received November 19, 1930)

Abstract

A thin ribbon of rhodium was subjected to rigorous heat treatment at 950°–1450°C for 1050 hours in a final vacuum of 10^{-8} mm of Hg in order to put it in a stable condition for photoelectric and thermionic measurements. During this period the long wave limit shifted from about 2530A to 3150A and then shifted back to 2509A where it remained during the latter 375 hours of heat treatment.

The photoelectric current was found to increase about 130% as a result of increasing the temperature of the rhodium from 25°C to 950°C. A rather sudden increase took place at about 240°C.

The photoelectric work function at 25°C was determined from the final long wave limit of 2482–2536A to be 4.92 ± 0.06 volts. The long wave limit at 240°C was 2652–2752A which gave a photoelectric work function of 4.57 ± 0.09 volts for this temperature. No further change in long wave limit was observed up to 650°C.

An anomaly was observed at 1100°C where the thermionic current was irregular and where the rate of change of the resistance of the rhodium with temperature changed on increasing the temperature.

The thermionic work function of rhodium, as determined from observations and with Richardson's equation, was 4.58 ± 0.09 volts. This value agrees with the photoelectric work function at 240°C.

Pure hydrogen and oxygen were introduced separately into the experimental tube while the rhodium was in its outgassed equilibrium condition. In the case of hydrogen the wave limit was changed from 2482–2536A to 2378–2482A. In the case of oxygen the wave limit was changed from 2482–2536A to a value so low that it could not be determined by the method used in this work.

AMONG the photoelectric and thermionic studies of metals which have been subjected to rigorous heat treatment, or distillation, there are: DuBridge's[1] extensive study of the thermionic and photoelectric properties of platinum; Cardwell's[2] work with iron and cobalt; Martin's[3] thermionic and photoelectric study of molybdenum; Warner's[4] work with tungsten; the work of Kazda,[5] Dunn,[6] and Hales[7] on mercury; and Goetz's[8] study of tin.

The object of this investigation has been (1) to investigate the photoelectric and thermionic properties of rhodium during and after subjection

[1] DuBridge, Nat. Acad. Sci. **12,** 162 (1926); Phys. Rev. **31,** 236 (1928); Phys. Rev. **32,** 961 (1928).
[2] Cardwell, Nat. Acad. Sci. **14,** 439 (1928); Nat. Acad. Sci. **15,** 544 (1929).
[3] Martin, Phys. Rev. **33,** 991 (1929).
[4] Warner, Nat. Acad. Sci. **13,** 56 (1927); Phys. Rev. **33,** 815 (1929).
[5] Kazda, Phys. Rev. **26,** 643 (1925).
[6] Dunn, Phys. Rev. **29,** 693 (1927).
[7] Hales, Phys. Rev. **32,** 950 (1928).
[8] Goetz, Phys. Rev. **33,** 373 (1929).

to rigorous heat treatment and (2) to introduce known gases in order to determine their effects upon the photoelectric properties of rhodium in the outgassed condition.

Apparatus

The experimental tube was similar to that used by DuBridge[9] with a few exceptions. Charcoal was not used in this work. Potential leads, spot-welded about a quarter of an inch below the ends of the filament, permitted the measurement of the P. D. across the filament. A grounded guard ring was installed between the collecting cylinder lead and all of the other leads of the experimental tube. The fact that Pyrex was sufficiently conducting at 100° C to prevent an accurate measurement of the photoelectric current immediately after cutting off the heating current made this device compulsory. The rhodium, purchased from the American Platinum Works, Newark, N. J. in the purest state that they could furnish, was in the form of ribbons 10 cm long by 0.4 cm wide by 0.004 cm thick. Each ribbon, bent in the form of a loop, was suspended inside a molybdenum collecting cylinder from two fifty mil tungsten leads through which current could be sent to heat the specimen to any desired temperature. All of these devices were enclosed in a Pyrex tube which was connected through two liquid air traps, a mercury cut-off, and a water-cooled mercury diffusion pump to a "Cenco" fore pump. The molybdenum cylinder was provided with two one half inch holes, one for illuminating the specimen and the other for pyrometric measurements of the temperature. A shutter, operated by an external magnet, could cover the opening through which the photo-active light had to pass. A quartz window, attached to the experimental tube by means of a graded quartz-Pyrex seal, served to admit radiation from a Cooper-Hewitt quartz mercury arc which was operated by a current of 3.1 amperes. The vertical arc was enclosed in a metal housing. Pressures lower than 10^{-6} mm of Hg were measured with an ionization manometer which was calibrated by extrapolating from data obtained by means of a McLeod gauge. The extrapolation was based on the work of Dushman and Found.[10] The photoelectric currents due to the full radiation of the mercury arc were measured by means of a Compton[11] electrometer shunted with a resistance of 10^9 ohms, thus permitting the use of the steady deflection method of measuring current. The sensitivity of the electrometer was determined at the time of each observation. The rate of charge method of detecting current was used in getting the long wave limit.

Outgassing Treatment

For 48 hours the molybdenum collecting cylinder was heated by electron bombardment in an auxiliary vacuum system at 800–1000°C before it was introduced into the experimental tube. When the experimental vacuum system was apparently free from leaks and the pressure was as good as could

[9] DuBridge, Phys. Rev. **29**, 451 (1927).
[10] Dushman and Found, Phys. Rev. **23**, 734 (1924).
[11] Compton, Phys. Rev. **14**, 85 (1919).

be read on the McLeod guage (of the order of 10^{-7} mm of Hg), the ionization manometer, the experimental tube, and the second liquid air trap were heated for 94 hours at approximately 400, 500, and 500 degrees C respectively. At the end of this period the pressure was again of the order of 10^{-7} mm of Hg while the tubes were hot. Then, in order to avoid excessive evaporation of the specimen, it was heated by a current at temperatures which were gradually increased from about 900°C to 1250°C and finally to 1450°C. The high vacuum end of the system up to the first liquid air trap was heated with a torch.

Fatigue

In Fig. 1 the photoelectric current due to the full arc is plotted as a function of the time of rest after cutting off the heating current. After fifty hours heating of the specimen there is a marked fatigue which becomes more pronounced until 250 hours of heating. Then it becomes rapidly less marked until

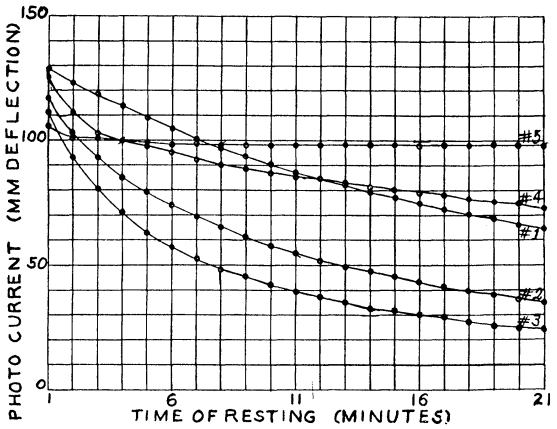

Fig. 1. Decrease of photoelectric sensitivity with time, using full arc.
Curve #1, taken after 50.5 hours of heat treatment.
Curve #2, " " 116.5 " " " "
Curve #3, " " 250.5 " " " "
Curve #4, " " 276.9 " " " "
Curve #5, " " 372.2 " " " "

there is practically no fatigue except for the first four or five minutes after cutting off the heating current. The drop in sensitivity during this short interval can be reasonably attributed to the fact that it required four or five minutes for the filament to cool to approximately room temperature. That this is the probable cause of the rapid initial change was shown by correlating the rate of cooling of the filament, as determined from resistance measurements, with the temperature change of photo-sensitivity. In determining a fatigue curve the first photoelectric observation was taken one minute after the heating current was stopped, and from the above mentioned comparison it was concluded that the filament was at this instant at a temperature of about 240°C. The change in the photo-current during the next

be read on the McLeod guage (of the order of 10^{-7} mm of Hg), the ionization manometer, the experimental tube, and the second liquid air trap were heated for 94 hours at approximately 400, 500, and 500 degrees C respectively. At the end of this period the pressure was again of the order of 10^{-7} mm of Hg while the tubes were hot. Then, in order to avoid excessive evaporation of the specimen, it was heated by a current at temperatures which were gradually increased from about 900°C to 1250°C and finally to 1450°C. The high vacuum end of the system up to the first liquid air trap was heated with a torch.

Fatigue

In Fig. 1 the photoelectric current due to the full arc is plotted as a function of the time of rest after cutting off the heating current. After fifty hours heating of the specimen there is a marked fatigue which becomes more pronounced until 250 hours of heating. Then it becomes rapidly less marked until

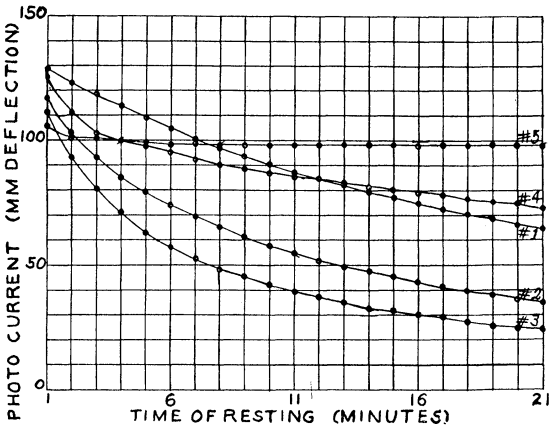

Fig. 1. Decrease of photoelectric sensitivity with time, using full arc.
Curve #1, taken after 50.5 hours of heat treatment.
Curve #2, " " 116.5 " " " "
Curve #3, " " 250.5 " " " "
Curve #4, " " 276.9 " " " "
Curve #5, " " 372.2 " " " "

there is practically no fatigue except for the first four or five minutes after cutting off the heating current. The drop in sensitivity during this short interval can be reasonably attributed to the fact that it required four or five minutes for the filament to cool to approximately room temperature. That this is the probable cause of the rapid initial change was shown by correlating the rate of cooling of the filament, as determined from resistance measurements, with the temperature change of photo-sensitivity. In determining a fatigue curve the first photoelectric observation was taken one minute after the heating current was stopped, and from the above mentioned comparison it was concluded that the filament was at this instant at a temperature of about 240°C. The change in the photo-current during the next

is not always possible to predict in advance the exact type of curve that will result when the temperature is decreased from 240°C to room temperature. The data for the curves in Figs. 3 and 4 were taken under apparently the same conditions, yet the final currents at room temperature are very different. In the case of the curve in Fig. 3—the more frequent type of curve —the final photo-current observed with zero heating current was not stable, but decreased in approximately one hour from the value at A to the value at B. Under the conditions of Fig. 4 on the other hand a stable condition was reached at once by the same gradual reduction of the heating current to zero. If the heating current was instantly reduced to zero when the filament was at about 1250°C (heating current of 12 amperes) the stable condition represented by B would always be reached in about 10 minutes. As mentioned above, almost half of this delay is accounted for by the time required for the filament and its surrounding cylinder to cool to room temperature. The behavior in the range from 240°C down depends also upon the vacuum conditions, a sequence such as that of Fig. 4 occurring only under the best conditions. The complicated situation which these curves suggest will be discussed later.

The Photoelectric Long Wave Limit

During the early stages of outgassing, the long wave limit was obtained by means of Corning glass filters. The final value, however, was located by using various solutions of tartaric acid, acetic acid, and the glass filters. Spectrograms of all filters were made at the same time that they were used. The wave limit was between 2378A and 2482A before any heat treatment. The specimen was heated for five hours at 500°C after which the long wave limit was between 2536A and 2752A. During the baking period of 94 hours it decreased to about 2536A. Then, on heating the rhodium at temperatures

Table I.

Time of heating specimen (hours)	Heating temperature (degrees C)	Long wave limit (angstroms)
25	900	2967
59	1025	2804–2967
81	1025	2804–2967
144	1025	2967–3341
190	1250	2967–3341
213	1250	(2536)–2752
267	1250	(2536)–2752
419	1250	2652–2752
676	1250	2482–2536
1051	1450	2482–2536

varying from 900°C to 1450°C, its long wave limit varied with time of outgassing as indicated in Table I. During the latter 375 hours the long wave limit remained between the 2482A and 2536A lines. Both of these lines are very intense and the limit could be very definitely located between them. If this limit is taken to be characteristic of outgassed rhodium, Einstein's[12] photoelectric equation gives for its photoelectric work function at 25°C

[12] Einstein, Ann. d. Physik **17**, 132 (1905).

$$V = \frac{ch\nu_0}{e} = \frac{c^2h}{e\lambda_0} = \frac{12335}{\lambda_0} = 4.92 \pm 0.06 \text{ volts},$$

where Birge's[13] values for the constants are used and λ_0 is (2482+2536)/2A. The long wave limit for the rhodium at approximately 240°C (corresponding to a heating current of 2.5 amperes) was found to lie between the 2652A and 2752A lines. The average of these values gives for the photoelectric work function at 240°C

$$V = \frac{12335}{2702 \pm 50} = 4.57 \pm 0.09 \text{ volts}.$$

No further change in long wave limit has been observed up to 650°C. Nevertheless, the photo-current continues to increase up to 950°C. An increase in temperature, therefore, appears to increase both the surface work function and the quantum efficiency.

Thermionic Current as a Function of Heating Current

The thermionic current was measured with a Leeds and Northrup galvanometer which had a sensitivity of 1.57×10^{-10} amperes per mm deflection at a scale distance of 1.5 meters. In Fig. 5 the thermionic current is plotted

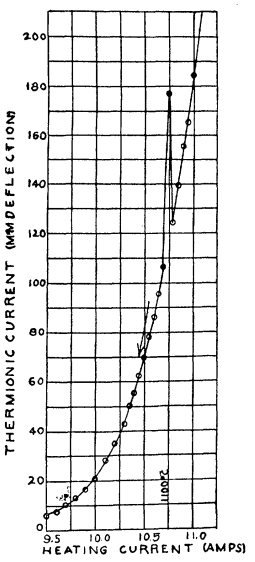

Fig. 5.

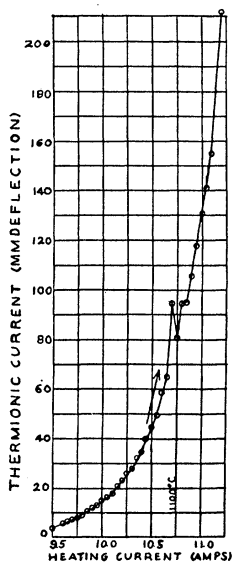

Fig. 6.

as a function of the heating current in amperes. The most interesting part of the curve is at approximately 10.7 amperes (about 1100°C) where the thermionic current is irregular. In the case of gradually decreasing the heating current and observing the thermionic current at short intervals of heating

[13] Birge, Phys. Rev. Supplement **1**, 1 (1929).

current, the writer has been able to obtain at about 10.7 amperes of heating current a gradual increase in the thermionic emission (heating current kept constant) until it reached a maximum value corresponding to an increase of temperature of approximately 25°C and then a gradual decrease in emission until equilibrium was reached at a value very close to what it was before the gradual increase began (see Fig. 6). This phenomenon indicates that at about 1100°C a change which liberates heat takes place on cooling rhodium.

Cardwell[14] published a similar thermionic curve for iron in which the thermionic current was irregular at 910°C, where the crystal structure changes from the body centered cubic to the face centered cubic type. One would think that the similar break in the thermionic curve for rhodium is due to the same cause; that is, to a change in the crystal structure. However, it is possible that the break is due to absorption or evolution of gas at this temperature. Nevertheless, it must be remembered that this specimen of rhodium had had more than 600 hours of heat treatment at about 1250°C in a final vacuum of 10^{-8} mm of Hg when the data for this curve were taken, and also that it has been impossible to detect any change in pressure peculiar

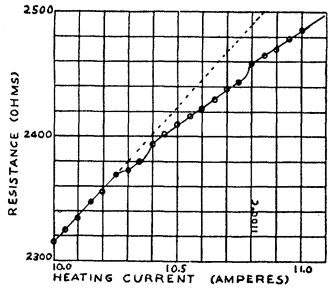

Fig. 7.

to this particular temperature while increasing or decreasing the heating current. The crystal structure of rhodium at various temperatures is now being determined in this laboratory by means of x-rays.

Mendenhall and Ingersoll[15] observed an anomaly at about 1050°C, consisting of an easily reversible change in the radiation of the surface of a small sphere of rhodium heated on a Nernst glower. They reported further that, as the temperature was lowered, the sphere became rather suddenly brighter —the change being seen to spread rapidly over the globule—and that, if the temperature was raised again, the reverse change took place. The fact that these observations were in air at normal pressure, while the present observations were in a very high vacuum, favors the view that the cause is a structure change rather than a gas action.

Resistance as a Function of Heating Current

In Fig. 7 the resistance of the specimen of rhodium is also plotted as a function of the heating current. It is interesting to observe that, at about

[14] Cardwell, Nat. Acad. Sci. **14**, 439 (1928).

[15] Mendenhall and Ingersoll, Phil. Mag. **15**, 205 (1908).

10.3 and 10.7 amperes of heating current, a definite change in slope occurs in the resistance curve. It is reasonable to suppose that the two breaks are due to uneveness of the temperature of the filament, because this curve was taken after the filament had been heated for 575 hours at approximately 1250°C. The fact that the slope of the resistance curve changes abruptly suggests the idea that a change in the structure may be taking place in the rhodium.

The Thermionic Work Function

The black-body temperatures of the rhodium strip were measured with a disappearing filament type of optical pyrometer which had been calibrated at the gold and palladium points and sectored down from the palladium point to the gold point. The readings were corrected for the transmission of the Pyrex window by means of data taken before it was sealed to the experimental tube. Then the true temperatures were computed from the relation

$$1/T - 1/S = \lambda \log \epsilon / c_2 \log e,$$

where T is the true temperature, S the apparent temperature, λ the wavelength used, ϵ the emissivity,[16] c_2 a constant in Wien's equation, and e the

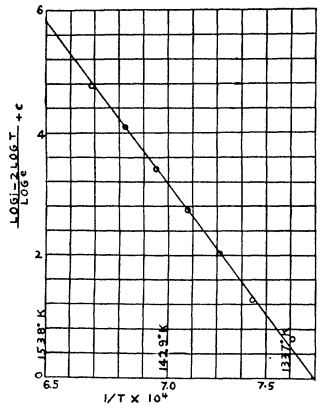

Fig. 8.

Naperian base. Fig. 8 gives the relation between $(\log i - 2 \log T)/(\log e) + C$ and $1/T$. The slope of this curve is the b in Richardson's relation

$$i = AT^2 e^{-b/T},$$

where i is the thermionic current and A is a constant.

$$b = 53{,}100° K.$$

Hence, the thermionic work function is

$$V = \frac{bk}{e} = \frac{53100 \times 1.371 \times 10^{-16} \times 299.8}{4.770 \times 10^{-10}} = 4.58 \text{ volts}.$$

[16] Bulletin of Bureau of Standards **11**, 595 (1914–15).

From other curves it is estimated that the result can be reproduced easily within 2%. Therefore, the thermionic work function is 4.58 ± 0.09 volts. This value agrees with the value given for the photoelectric work function at 2.5 amperes of heating current (approximately 240°C).

The Effect of Pure Hydrogen and Oxygen on Outgassed Rhodium

Extreme care was given to the purification of the hydrogen and oxygen used in this work. Hydrogen, admitted to the experimental tube after 500 hours of heat treatment for the rhodium, changed the long wave limit from the equilibrium value of 2482–2536A (a value characteristic of rhodium after 1000 hours of heat treatment in a final vacuum of 10^{-8} mm of Hg) to 2378–2482A; that is, the limit was changed to approximately the original value characteristic of the specimen before it had received any heat treatment. The photo-current was decreased very quickly from 100 mm deflection to 2 mm. Heating the specimen at 1000°C for one minute in hydrogen at a pressure of one mm of Hg increased the photo-current from 2 mm to 100 mm deflection, but the photo-sensitivity dropped to 3 or 4 mm in 4 minutes after reducing the heating current to zero. Allowing the pumps to remove as much of the hydrogen as possible without heating the rhodium increased the photo-current from 2 mm to 4 mm. Light from the mercury arc increased the photo-current from 2 mm to 4 mm in two hours. The long wave limit characteristic of the rhodium after 1000 hours of heat treatment was attained in 100 hours of heating at 1250°C after this exposure to hydrogen. It is evident that rhodium occludes and adsorbs hydrogen quite well since its photoelectric properties are radically affected by the presence of hydrogen.

Oxygen, admitted to the system after the specimen had regained its stable condition after the introduction of hydrogen, changed the long wave limit from its equilibrium value of 2482–2536A to a value below 2300A. Oxygen was more effective in decreasing the long wave limit than hydrogen. Heating the specimen at 1000°C for one minute in oxygen at a pressure of 1 mm of Hg did not restore the photo-current to its original 100 mm deflection. In order to attain stable conditions again it was necessary to heat the specimen at 1250°C for 100 hours and to heat by means of a torch the high vacuum end of the system several times during this interval.

The following peculiarities of the photoelectric behavior below 240°C require further consideration:

(1) The stable value of the work function at room temperature is 4.92 volts; at 240°C this has changed to 4.57 volts, but no further change is observed from there on up to 650°C.

(2) When the rhodium was cooled as rapidly as possible from 1250°C to room temperature, the stable condition would be reached in 10 minutes after stopping the heating current.

(3) When the temperature was varied slowly from above 240°C, the more usual form of ascending and descending photo-current curve is shown in Fig. 3. Condition *A* is not stable, but changes to *B* in the course of an hour.

(4) Under the best attained vacuum conditions (10^{-8} mm of Hg) a different cycle is observed (Fig. 4) and with the same rate of change of temperature as in Fig. 3, the stable condition (B) is reached at once.

(5) It is to be noticed that the better the vacuum (Fig. 4) the more sudden are the changes in photo-current with temperature.

The question is, are these peculiarities caused by changing surface contamination, or do they indicate a structure change in the rhodium occurring at or below 240°C? A simple calculation shows that with a pressure of 10^{-8} mm of Hg and assuming no molecular reflection, it would take from one-half to several hours to form a monomolecular layer on the metal, according to the density one assumes for the gas layer. Hence from (2) above it does not seem likely that condition B is due to a gas covered surface, unless the gas layer is stable at high temperatures (1250°C) as well as at room temperature, being perhaps a hydride. Furthermore, in order to account for (1) and (3) this gas layer or hydride must be assumed to be unstable from 240°C up to some higher temperature, the relatively rapid rise in the ascending curve of Fig. 3 being due to the breaking up of the layer. But this does not fit (5), for the sudden drop in the descending branch of Fig. 4 would have to be attributed to the partial formation of the layer, and such rapid formation would be *less* likely to occur under the extremely high vacuum conditions of Fig. 4 than under the somewhat lower vacuum conditions of Fig. 3—which is contrary to fact. The sudden changes so prominent in Fig. 4 strongly suggest that there is an allotropic change at 240°C, and that the structure stable above this temperature can be carried down to lower temperatures in an irregular way, depending upon circumstances. A comparison of Figs. 3 and 4 suggests furthermore that the influence of this change in structure can be easily obscured by changing contamination except under the very best vacuum conditions. This is, however, not a completely satisfactory interpretation of the results.

In conclusion, the writer wishes to express his sincere thanks to Dr. C. E. Mendenhall, under whose direction this work has been done, to Mr. J. B. Davis, the glass-blower, and to Mr. J. P. Foerst, the mechanician.